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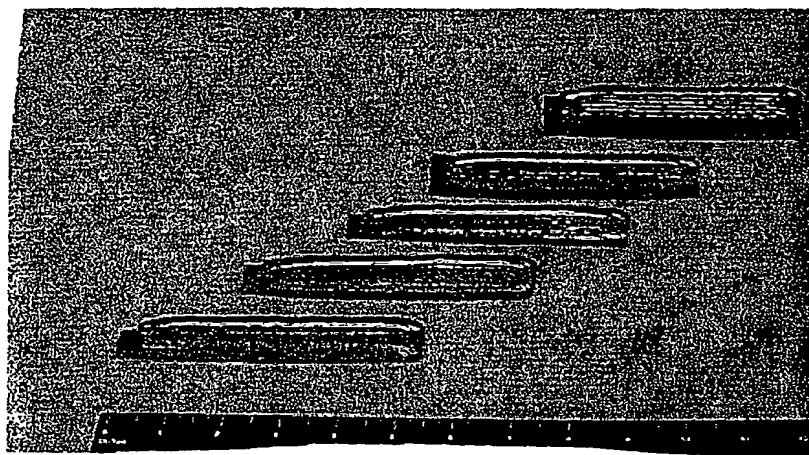
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(54) Title: REFRACTORY METAL AND ALLOY REFINING BY LASER FORMING AND MELTING



Sample 1
Sample 2
Sample 3
Sample 4
Sample 5

(57) Abstract: A process to chemically refine and consolidate tantalum, niobium and their alloys to a fabricated product of net shape or near-net shape with higher throughput, more consistency, and lower manufacturing costs compared to prior art routes or rejuvenate damaged and deteriorated refractory metal parts. Powder metal is loaded into hoppers to be fed into laser forming/melting equipment. A suitable substrate is loaded into a laser forming/melting chamber onto which the powder will be deposited and consolidated in a point-scan process. As the powder is fed onto successive points of the surface of the substrate in linear traces, the laser is used to heat and partially melt the substrate and completely melt the powder. A combined deposition and melt beam traces the substrate surface repeatedly over a selected area to build up a dense coating of controlled microstructure in multiple layers. A fully dense deposit is built up that becomes the desired shape.

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REFRACTORY METAL AND ALLOY REFINING BY
LASER FORMING AND MELTING

5

BACKGROUND OF THE INVENTION

The present invention relates to fabrication and rejuvenation of refractory metal parts, and more particularly to fabrication and
10 rejuvenation of refractory metal parts at net shape or near shape with controlled microstructure.

Current processes for producing high purity refractory metal parts, such as sheets made from tantalum and tantalum alloys (for usage as sputtering targets, tube performs, furnace part performs, etc.), include
15 powder and ingot metallurgy. The ingot metallurgy process begins with selecting and blending suitable powders, pressing into bars and sintering. An electron beam or plasma or arc furnace is used to melt the bar and cool it into an ingot. The melting can be done in multiple steps. Electron beam melting and remelting removes impurities to produce an essentially
20 pure tantalum ingot. Purities of 99.9% tantalum are routinely achieved. The ingot is thermomechanically processed and further cold or hot worked as needed (or cold worked with intermediate annealing) to produce a desired shape, such as plate, sheet, rod or fabricated part (hemisphere, semi-hemisphere, conical, dished sheet, cup, box, etc.). Components
25 may also be machined directly from ingots 3.

This overall process is relatively slow and results in a final yield of approximately 40 to 60 percent. The sintering process consumes a significant amount of furnace time, but it is required to provide sufficient mechanical strength in the bars and is a preliminary deoxidation step for
30 the refractory metal powder, such as tantalum. The bars are usually electron beam-melted under a hard vacuum to remove chemical impurities. The electron beam melting process can also consume a significant amount of furnace time and power, such as three electron

beam guns at 105 kilowatts for 8 to 16 hours. Remelting is usually required which also consumes significant furnace time and power, such as four electron beam guns at 150 kilowatts for 8 to 16 hours.

5 Laser additive manufacturing (LAM) is a direct deposition process that uses a high power laser and powder feeding system to produce complex three-dimensional components from metal powders. The high power laser and multi-axis positioning system work directly from a CAD file to build up the component using a suitable metal powder. This process is similar to conventional rapid prototyping techniques, such as
10 stereolithography and selective laser sintering (SLS), and laser welding. Laser welding was developed to join two components or to fabricate an article integral to a component. However, a fully dense metal component can only be made with such additional steps as casting or HIP'ing (hot isostatic pressing). Such a laser
15 process has been developed to manufacture near-net shape titanium components for the aerospace industry. But a process does not exist for still higher melting refractory metals, such as tantalum.

Additionally, sputtering targets of high temperature materials, such as tantalum and other refractory metals (Ta, Nb, Ti, Mo, Zr, metals and
20 alloys; hydrides, nitrides and other compounds thereof) used in integrated circuit manufacture and other electrical, magnetic and optical product manufacture usually are eroded in a non-uniform way during the process of sputtering which leads to a race track like trench on the operating side of the target. In order to prevent any contamination of substrates or
25 catastrophic break-through of coolant fluids behind the target, the targets generally are withdrawn from service well before the refractory sputter metal is penetrated, accepting the need for a new target after only a minor portion of the sputter metal has been consumed. The major part of the sputter target can be resold only at scrap price or recycled with difficulty
30 and apart from this, the backing plate of the target needs to be removed and may be re-bonded to a new sputter metal plate for recycling.

Consequently, there is a need to rejuvenate the refractory metal of the sputtering target to eliminate the need to recycle the whole target after only a minor share of the tantalum plate has been consumed.

It is an object of the present invention to provide a laser processing
5 method for refractory metals and their alloys that produces a fully dense deposit that can be planar or curved with macro- and micro-mechanical properties at least equivalent to traditionally melted, consolidated, rolled and annealed parts.

It is a further object to increase yield recovery and otherwise
10 decrease fabrication time and costs by net-shape or near-net shape fabrication.

It is a further object of the invention to decrease the recycling cost of refractory metal parts, such as tantalum plates for sputtering targets including their backing plate.

15 It is yet another object of the invention to reduce the cycle time between removing the refractory metal part, such as a sputtering target, from service and getting it back to service will be shortened.

SUMMARY OF THE INVENTION

20 The invention relates to a process for making a refractory metal part comprising (a) loading powder metal particles into a hopper for feeding into a laser additive chamber, (b) loading a substrate into the laser additive chamber, (c) feeding the powder metal powders into the additive chamber onto successive points on the substrate in a linear trace, (d)
25 melting the substrate and the powder with a laser beam and building up multiple coatings of a controlled microstructure, (e) tracing the substrate over a selected area with a combined deposition and melt beam and building up a coating of a controlled microstructure in multiple layers, and
30 (f) building up a deposit from the coating and forming a refractory metal part.

The invention also relates to a method for rejuvenating a tantalum sputtering target comprising subjecting an eroded region of a tantalum sputtering target to plasma deposition, forming a fully dense coating, and thereby rejuvenating the tantalum sputtering target.

5 The invention also relates to a method for rejuvenating a tantalum sputtering target comprising subjecting an eroded region of a tantalum sputtering target to laser sintering, forming a fully dense coating, thereby rejuvenating the tantalum sputtering target.

10 The invention also relates to a method for rejuvenating a tantalum sputtering target comprising subjecting an eroded region of a sputtering target to hot isostatic pressing, forming a fully dense coating, and filling the eroded region of a tantalum sputtering target, thereby rejuvenating the tantalum sputtering target. Alternatively, the invention can also include products made from such processes.

15 As such, the present invention is a process and the resultant product. The process is one to chemically refine and consolidate refractory metals and their alloys to a fabricated product of net shape or near-net shape with higher throughput, more consistency, and lower manufacturing costs compared to prior art routes. Powder metal is
20 loaded into hoppers to be fed into the LAM equipment. A suitable substrate is loaded into a LAM chamber onto which the powder will be deposited and consolidated in a point-scan process. As the powder is fed onto successive points of the surface of the substrate in linear traces, the laser is used to heat partially melt the substrate and partially or
25 completely melt the powder. A combined deposition and melt beam traces the substrate surface repeatedly over a selected area to build up a dense coating of controlled microstructure in multiple layers. A fully dense deposit is built up that becomes the desired shape. This entire process is conducted in a chamber under inert conditions, such as argon, at, near or
30 below atmospheric pressures but can also be conducted under a hard vacuum.

The relatively high heat or power input to the powder particles and the short diffusion distance results in purification of the powder and the resultant product. The process yields are 90 percent or more, requiring minimal machining to clean up deposit edges and product surfaces depending on final shape and end use application.

As used in the manufacture of sputtering targets, the process will yield the necessary grain purity and have a columnar grain structure to aid uniform sputtering characteristics.

For rejuvenation purposes, the race track trench on the face of the deteriorated tantalum sputtering target is filled by laser sintering, plasma deposition or HIP-bonding powder/plate material which will yield a fully dense coating. In the case of laser sintering or plasma deposition the target could be rejuvenated without debonding the backing plate from the target. In the case of HIP-bonding either low oxygen Ta powder or any Ta plate material could be used. Rejuvenation is an economic process if filling the trench by any of the proposed methods is cheaper than recycling the whole target. No debonding of the backing plate is needed. It can be reused as many times as desired.

Used sputtering targets can be processed to fill the race track trench or other erosion zone on the face of the target by a placement or deposition of sputter metal and sinter bonding by laser or EB heating for sintering, plasma discharge coupled with deposition or HIP-bonding powder/plate material. Use of these methods will yield a fully dense coating. This avoids the need for decoupling the tantalum from the copper, filling the erosion zone of the tantalum plate with tantalum powder and HIP bonding and reassembly. In the case of laser or EB scan sintering or plasma discharge coupled with deposition the target can be rejuvenated without separating the backing plate from the target.

The various forms of rejuvenation produce a filled erosion zone with microstructure similar to the balance of the target.

The rejuvenation of a refractory metal (e.g. tantalum) target eliminates the need to recycle the whole target after only a minor share of the sputter plate has been consumed. Such rejuvenation can be more economical than recycling the whole target. No separation of the bonded
5 backing plate (e.g. copper) is needed.

This rejuvenation can be reused as many times as desired. Other objects, features and advantages will be apparent from the following detailed description of preferred embodiments taken in conjunction with the accompanying drawings in which:

10

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 shows the five deposits (products) formed from the preferred embodiments of the process of the invention;

Fig. 2 shows a typical metallographic section taken from each such
15 deposit;

Fig. 3 shows a cross section of typical target and backing plate;

Fig. 4 shows a face view including a usual erosion goal;

Fig. 5 is a block diagram of the rejuvenation process; and

Fig. 6 shows in outline form a vacuum or inert gas chamber set-up
20 for practice of the invention.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

An embodiment of the present invention is a laser process to produce high purity refractory metal and alloys formed from refractory
25 metal powder. The tantalum powder (-120+325 mesh), and a tantalum plate substrate applied in a depositing apparatus as described in U.S. 6,269,536, incorporated herein by reference in its entirety). The laser energy was approximately 17 kW delivered. Figure 1 shows the five deposits formed from the laser process. Each deposit is the result of
30 approximately five to seven layers with each layer being approximately 0.010" thick.

The physical property differences described above also meant the deposition rates had to be much lower than for titanium. The higher melt temperature and thermal conductivity of tantalum compared to titanium meant the tantalum molten pool was probably smaller and a smaller

5 quantity of powder could be melted by the available laser power.

Table 1 shows the results of the chemical analysis (GDMS) of the starting powder and the final deposits. In general there was very little change in the refractory metal content (example, Nb, and W) of the deposit as compared to the starting powder. With the exception of titanium

10 and vanadium, there was a measurable reduction in the metallic contamination of the deposit. Titanium and vanadium contamination came from previous work in the test equipment conducted with Ti-6Al-4V alloy.

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30

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Table 1

	Concentration (ppm)	Concentration (ppm)	
Element	Powder	Deposit	PPM Reduction Powder-Deposit
B	0.18	0.04	0.14
Mg	35	0.21	34.79
Al	1.4	0.46	0.94
Si	30	4.2	25.80
P	1.1	0.1	1.00
Ti	0.9	30	(-29.10)
V	0.1	3.1	(-3.00)
Cr	3.8	1.4	2.40
Mn	0.8	0.07	0.73
Fe	50	4.5	45.50
Co	0.47	0.07	0.40
Ni	700	29	671.00
Cu	4.6	0.05	4.55
Nb	91	90	1.00
Mo	1.8	0.44	1.36
W	2.6	2.4	0.20
%Ta	99.908	99.983	----
Total	925	166	759

Figure 2 shows a typical metallographic section taken from each deposit. No porosity was found in any of the sections examined except at the very outer surface of the deposit. The deposits examined had from two to five grains (grain boundaries are marked with arrows) across their
5 width.

These grains grew from the original grains in the base plate. There was no evidence of any internal defects (i.e., cracks, inclusions, foreign particles, and the like) in the deposits.

Tables II and III show the mechanical test results. The Vicker's
10 Hardness Numbers (VHN, 500g) for three of the samples are slightly higher than might be expected for rolled and annealed tantalum sheet (VHN of approximately 100). These deposits have not been annealed and the VHN suggests the material is not brittle. The slightly higher hardness of sample 1 as compared to samples 2 and 3 is the result of its slightly
15 higher oxygen content. Table III shows the room temperature yield and ultimate strengths of these three deposits meet the ASTM specifications for rolled and annealed tantalum sheet. The samples 1, 2, and 3 there are acceptable, notwithstanding the elongation values are slightly below specification minimums (note that sample 3 failed near the radius of the
20 test bar, not in the center of the gage section, and was deemed a bad test).

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30

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Table II - Vicker Hardness Numbers, 500a

Sample 1	Sample 2	Sample 3
121.7	114.0	109.8
120.0	106.6	109.2
125.4	107.4	110.7
125.0	106.6	108.3
124.3	106.6	111.6
123.2	111.5	110.7
121.1 123.6	111.7	110.1
121.4	105.4	109.9
121.1	112.1	106.8
123.5	110.0	106.2
Avg. 122.9 \pm 1.8	109.2 \pm 3.0	109.3 \pm 1.7

Table III – Room Temperature Tensile Test Results

Sample No.	Yield Strength (ksi)	Ultimate Tensile Strength (ksi)	Total Elongation
1	29.7	31.7	24.1
2	25.9	31.5	23.5
3	26.4	30.0	12.7
ASTM B365 (mins.)	15.0	25.0	25.0

10 The results presented above show the laser formed tantalum deposits have chemical and mechanical properties equivalent to rolled and annealed tantalum sheet. The deposits were fully dense with no evidence of porosity except at the very outer surface of the deposit.

The rejuvenation of refractory metal parts is illustrated in Figs. 3-6. Figs. 3-4 show a tantalum (Ta) sputter plate bonded to a copper (Cu) backing plate which may include additional complexity such as bonded-on water cooling coils (CL) or even be part of a large cooling liquid reservoir and/or have complex flanges and mechanical and electrical attaching structures.

E indicates a typical race track form erosion zone arising from sputtering usage.

Fig. 5 is a flow chart of implementation of the present invention. A vacuum or inert gas zone is established for a used Ta-Cu target assembly. The erosion zone (E-Zone) is filled with powders of the sputter metal that is bonded by laser or electron beam (EB) raster scanning to melt powder surfaces, but not complete particles. The melting can be done during powder deposition or after deposition on a layer-on-layer basis.

A powder derived foil can also be pre-made and laid into the trench.

In all cases the fill is sintered for self bonding and adhesion to target and leveled off by machining, sanding or other abrasion etching and/or a burn-in sputtering process.

The following are several detailed ways of rejuvenating a refractory part. As shown in Fig. 6 such a plate can be placed in a vacuum chamber (VC) evacuated atmospheric pressure purified inert gas (argon) atmosphere utilizing conventional pump P and gas back-fill apparatus G with valving V. A powder feeder comprising multiple nozzles can insert multiple high velocity streams of Ta powder of -100 to 325 mesh to the erosion zone (region). The powder feeder can scan along the erosion zone or the target can be moved relative to a fixed powder feeder. A 15-20 KW (preferably 20-25 laser beam LB formed by a case C and conventional scan optics M1, M2 which can be wholly in the chamber or, partly outside the chamber using a window for beam passage can be traced in raster scan fashion over the erosion zone, as the powder falls, to melt powder particle surfaces and enable particle to particle bonding and

bonding to the base of the erosion zone continuously and repeatedly around the zone until it is filled. Powder mass calculations and/or optical monitors can be used to determine completion and a cut-off of filling. The laser can provide post-fill heating to complete the sintering. Separate
5 target heaters can be used to preheat the target or provide additional heat during the rejuvenation.

One form of equipment usable for fabricating and rejuvenating refractory metals is the Lasform brand direct metal deposition system of AeroMet Corp., as described, e.g., in Abbott et al., "Laser Forming
10 Titanium Components" in the May 1998 issue of Advanced Metals & Processes and Arcella et al., "Producing Titanium Aerospace Components From Powder Using Laser Forming," Journal of metals (May 2000), pp. 28-30.

The invention can also be applied to other refractory powder
15 metals, such as Re, W, Mo, W alloy, Mo, alloy, RE alloy, niobium, tantalum alloys, and niobium alloys.

It will now be apparent to those skilled in the art that other embodiments, improvements, details, and uses can be made consistent with the letter and spirit of the forgoing disclosure and within the scope of
20 the invention.

WHAT IS CLAIMED IS:

1. A process for making a refractory metal part comprising:
 - (a) loading powder metal particles into a hopper for feeding into a laser additive chamber,
 - 5 (b) loading a substrate into the laser additive chamber,
 - (c) feeding the powder metal powders into the additive chamber onto successive points on the substrate in a linear trace,
 - (d) melting the substrate and the powder with a laser beam and building up multiple coatings of a controlled microstructure,
 - 10 (e) tracing the substrate over a selected area with a combined deposition and melt beam and building up a coating of a controlled microstructure in multiple layers, and
 - (f) building up a deposit from the coating and forming a refractory metal part.
- 15 2. The process of Claim 1, wherein the deposit built up from the coating is a fully dense deposit.
3. The process of Claim 1, wherein the process is carried out under inert conditions.
4. The process of Claim 3, wherein the conditions include argon,
20 at or near or below atmospheric pressure.
5. The process of Claim 1, wherein the process is carried out under a hard vacuum.
6. The process of Claim 1, wherein the laser beam generates sufficiently high heat to create conditions that purify the powder and the
25 refractory metal part.
7. The process of Claim 1, wherein the refractory metal part is a sputtering target.
8. A refractory metal part made by the process of Claim 1.
9. A method for rejuvenating a tantalum sputtering target
30 comprising subjecting an eroded region of a tantalum sputtering target

to plasma deposition, forming a fully dense coating, and thereby rejuvenating the tantalum sputtering target.

10. The method of Claim 9, wherein the tantalum sputtering target has a backing plate and the target is rejuvenated without
5 debonding the backing plate from the target.

11. A sputtering target made by the method of Claim 9.

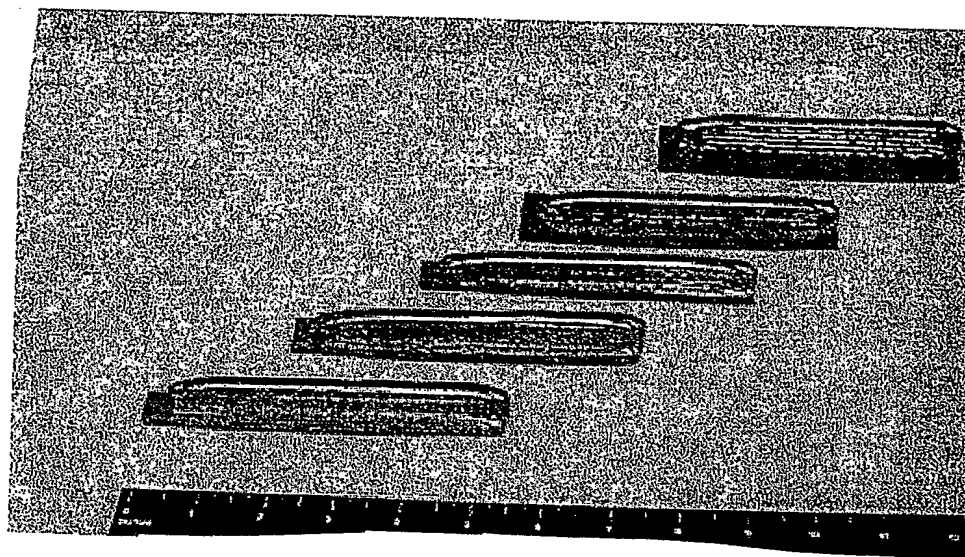
10. A method for rejuvenating a tantalum sputtering target comprising subjecting an eroded region of a tantalum sputtering target to laser sintering, forming a fully dense coating, thereby rejuvenating the
10 tantalum sputtering target.

11. The method of Claim 10, wherein the tantalum sputtering target has a backing plate and the target is rejuvenated without debonding the backing plate from the target.

12. A sputtering target made by the method of Claim 10.

15 13. A method for rejuvenating a tantalum sputtering target comprising subjecting an eroded region of a sputtering target to hot isostatic pressing, forming a fully dense coating, and filling the eroded region of a tantalum sputtering target, thereby rejuvenating the tantalum sputtering target.

20 14. A sputtering target made by the method of Claim 13.



Sample 1
Sample 2
Sample 3
Sample 4
Sample 5

FIG. 1

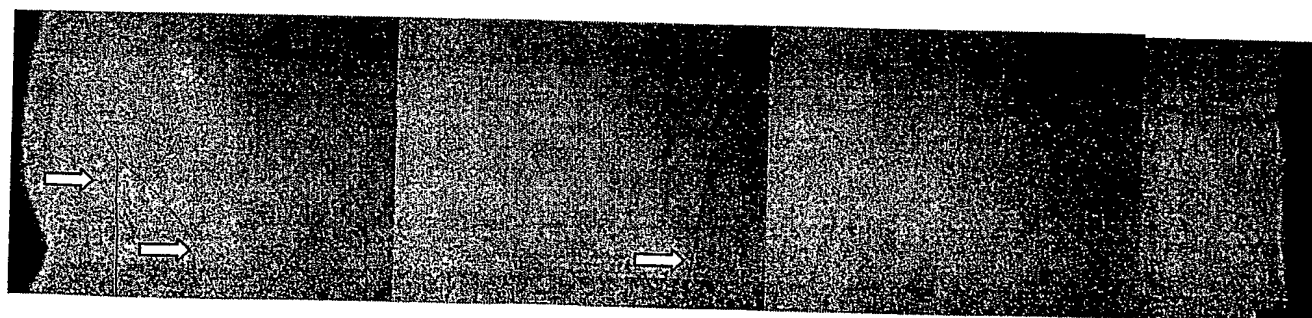


FIG. 2

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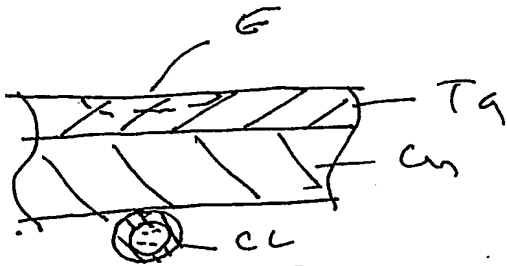


Fig. 3

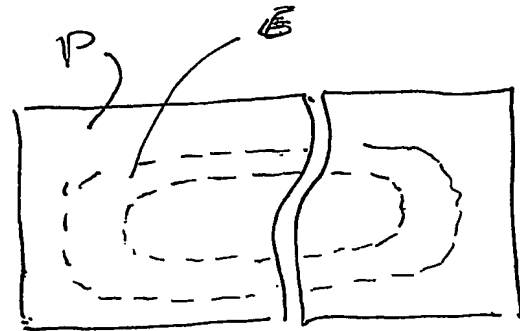


Fig. 4

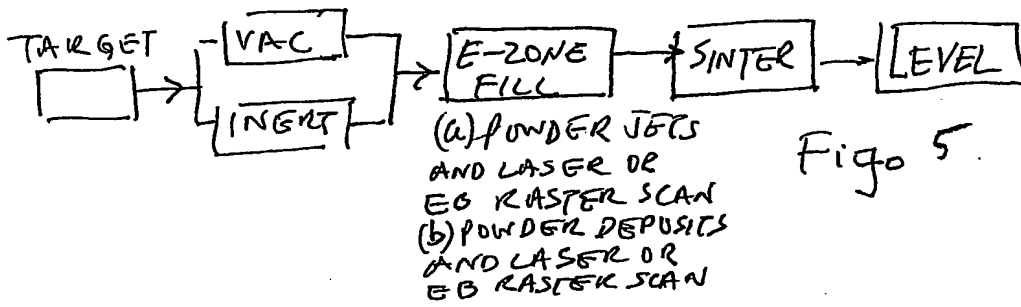


Fig. 5

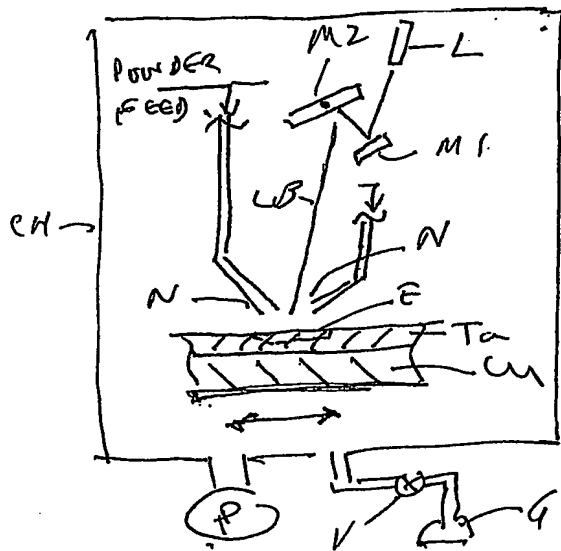


Fig. 6

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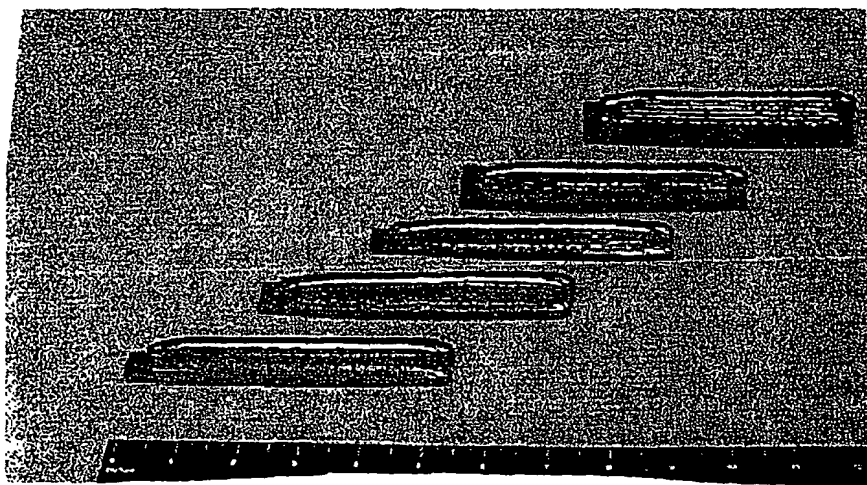
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C23C26/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, IBM-TDB, INSPEC, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	ABBOTT D H ET AL: "LASER FORMING TITANIUM COMPONENTS" ADVANCED MATERIALS & PROCESSES, AMERICA SOCIETY FOR METALS, METALS PARK, OHIO, US, vol. 153, no. 5, May 1998 (1998-05), pages 29-30, XP001120282 ISSN: 0882-7958 cited in the application the whole document --- -/--	1-6,8

☒ Further documents are listed in the continuation of box C.☐ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

16 May 2003

Date of mailing of the international search report

01.08.03

Name and mailing address of the ISA

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Brisson, O

INTERNATIONAL SEARCH REPORT

PCT/ISA/210
03/01825

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	ARCELLA F. G., FROES F. H.: "Producing titanium aerospace components from powder using laser forming" JOM, MINERALS, METALS & MATERIALS SOC (TMS), WARRENDALE, PA, USA, May 2000 (2000-05), pages 28-30, XP001157479 ISSN: 1047-4838 cited in the application the whole document	1-6,8
X	GRIFFITH M. L. ET AL: "UNDERSTANDING THE MICROSTRUCTURE AND PROPERTIES OF COMPONENTS FABRICATED BY LASER ENGINEERED NET SHAPING (LENS)" MATERIAL RESEARCH SOCIETY SYMPOSIUM PROCEEDINGS, SOLID FREEFORM AND ADDITIVE FABRICATION - 2000 CONF., SAN FRANCISCO, CA, USA, vol. 625, 24 - 26 April 2000, pages 9-20, XP001157465 ISSN: 0272-9172 the whole document	1-6,8

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 03/01825

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-8

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1-8

A process for making a refractory metal part by supplying a metal powder feed to a laser focal zone close to the surface of a substrate, where the powder is at least partially melted and resolidified to form a film. The product obtainable thereof.

2. Claims: 9-11

a method for rejuvenating a tantalum sputtering target involving the use of a plasma and the rejuvenated tantalum sputtering target obtainable thereof.

3. Claims: 12-14

a method for rejuvenating a tantalum sputtering target by laser sintering and the rejuvenated tantalum sputtering target obtainable thereof.

4. Claims: 15-16

a method for rejuvenating a tantalum sputtering target by subjecting an eroded region of a sputtering target to hot isostatic pressing and the rejuvenated tantalum sputtering target obtainable thereof.